

**TITLE: SUPERCONDUCTING TAPES****FIELD OF THE INVENTION**

The present invention relates to a superconducting tape and in particular to a composite superconducting tape.

5       The invention has been developed primarily for use with high load current carrying cables and will be described hereinafter with reference to that application. It will be appreciated, however, that the invention is not limited to this particular field of use.

**BACKGROUND OF THE INVENTION**

10       It is known to use superconducting tapes to make coils, magnets, transformers, motors and generators as well as current carrying cables. Superconductors are materials which exhibit, at sufficiently low temperatures, substantially zero electrical resistance for direct current. The temperature at which a substance becomes superconducting is called the transition or critical temperature. Early superconductors had critical temperatures  
15 that necessitated refrigeration with liquid helium. However, due to low thermodynamic efficiency, this is an expensive and generally uneconomic arrangement. More recently it has been known to utilise "ceramic" superconductors with critical temperatures up to around 135K.

Superconductors with critical temperatures over 77K are of particular interest as  
20 they can be operated with liquid nitrogen refrigeration at relatively high thermodynamic efficiency and relatively low cost.

Superconductors can only carry so much current before the voltage drop per unit of length begins to increase in an exponential form. The so called "critical" current,  $I_c$ , is defined for precision as the maximum current that can be carried before the voltage drop  
25 increases above 1 microvolt per centimetre.

Tapes comprising superconducting material, and referred to as superconducting tapes, are already known, and comprise one or many superconducting filaments in a medium of silver or silver alloy. The main class of superconducting tape are known as powder-in-tube or PIT tape. These are made by drawing or otherwise reducing a tube of  
30 silver or silver alloy filled with a powder form of the superconducting oxide or its precursor. The tubes are also rolled or otherwise formed into a thin tape.

Multifilamentary tapes are mostly made by grouping filled tubes in a common silver or silver alloy sheath at an intermediate stage of reduction.

One important superconducting oxide is known as Bi-2223, and is a compound oxide of bismuth, strontium, calcium and copper. Certain limited substitutions can be made, as required. Bi-2223 can also be considered a cuprate salt.

Known tapes usually have a thickness of between around 0.2 mm and 0.3 mm, and a width of between 2 mm and 5 mm. The superconducting filaments must be thin to obtain an adequate critical current and are typically around 10 to 40 microns in thickness. Moreover, the filaments typically have an aspect ratio of at least 1:10.

10 The filaments comprise many plate-like grains and, for good performance, the grains should be aligned as much as possible in the same crystallographic orientation. The relative orientation is often referred to as the grain alignment or "texture". Well textured filaments allow a high critical current, and give overall flexibility to the whole tape. If the filaments are too thick, then they will degrade at relatively large bending  
15 radii of the tape.

A superconducting tape's flexibility can be measured in terms of the reversible bending radius achievable when such bending is carried out at room temperature. The reversible bending radius may be defined as the largest bending radius which causes more than 5% degradation in the critical current,  $I_c$ , as measured on the unstrained tape.

20 Other criteria which are used to define the quality of the tape and the amount of current that a superconducting tape can carry is the critical current density,  $J_c$ , and the engineering current density,  $J_e$ . The critical current density,  $J_c$ , is defined by  $J_c = I_c / A_{sc}$ , where  $A_{sc}$  is the total superconductor area in the cross-section of the tape, and the engineering current density  $J_e$  is defined by  $J_e = I_c / A_{tape}$ , where  $A_{tape}$  is the total cross-  
25 sectional area of the tape. The higher  $J_c$  and  $J_e$  the better. The ratio of the cross-sectional area of the superconductor to the cross-sectional area of the whole tape is called the Fill Factor, FF, and, therefore, we can deduce that  $FF = J_e / J_c$ .

When tapes are used to carry alternating current, rather than direct current, the superconducting tapes do not exhibit zero power loss, though losses are small compared  
30 to those exhibited by normal metallic conductors. This power loss resulting from the carrying alternating current rather than direct current is called "AC loss".

For an individual tape, the AC loss can be of the order of 100 microwatts per metre per Amp of critical current squared. To achieve the maximum performance from these tapes the AC losses should be minimised. This is particularly true when they are used in superconducting cables where the current loads are high.

5 Composite tapes are sometimes made by forming a stack of individual tapes and wrapping the stack with one or more flexible wrapping tapes to keep it together. These wrapping tapes are generally a metal and more often silver.

Inevitably there are some gaps and/or overlapping between the turns of the wrapping tape. If such a wrapped stack were to be rolled then the gaps or overlapping  
10 would create kinks in the filaments, which destroys local grain alignment leading to degradation of the overall critical current density  $J_c$ .

It is an object of the present invention, at least in the preferred embodiment, to overcome or substantially ameliorate one or more of the disadvantages of the prior art, or at least to provide a useful alternative.

#### 15 DISCLOSURE OF THE INVENTION

According to a first aspect of the invention there is provided a composite superconducting tape comprising a multiplicity of stacked and diffusion bonded superconducting monofilamentary or multifilamentary tapes and in which all elongate components extend longitudinally.

20 The preferred embodiments of the invention making use of the combination described above to achieve a tape of high superconductor cross-sectional area and a thin and wide filament structure. This is highly desirable for a high critical current density.

Preferably, the filament thickness is as thin as is required to provide a desired critical current density, wherein the fill factor of the tape is about 40%.

25 Preferably also, the composite tape consists solely of the stacked and bonded constituent tapes. The composite tape has exposed major surfaces which are defined by those surfaces of the constituent tapes which are not abutted against an adjacent surface. More preferably, the exposed major surfaces of the composite tape covered with a metal. More preferably, the tape is of silver or silver alloy. In other embodiments, metal tapes  
30 other than those of silver are used.

In a preferred form, the superconductor filaments are at least 10 $\mu$ m away from the exposed major surfaces. More preferably, use is made of the thin metal tape to allow this to be achieved without incorporating unnecessary amounts of silver elsewhere in the composite tape.

5 Preferably also, the metal tape is used to control mechanical stresses. More particularly, some composite tapes are intended, in use, to be curved always in one direction such that one of the major exposed surfaces will always be convex and the opposed major exposed surface will always be concave. In such circumstances a metal tape is applied to the major surface that will be convex. More preferably, the major side  
10 that will be concave either does not include a metal tape or includes a second metal tape that is weaker than the first metal tape. In some embodiments the stronger tape is a silver alloy tape and the weaker tape a pure silver tape. In other embodiments the tapes differ in thickness.

Preferably, the metal tape is flat has a width not substantially greater than that of  
15 the superconducting tapes. In some embodiments the metal tape has a width of less than the superconducting tapes. In still further embodiments a wider metal tape is used which is, or subsequently becomes, bent to a channel section. The latter arrangement has structural advantages but adversely affects fill factor. Other embodiments utilise a silver foil or other compatible material which is wrapped around the stack but extending  
20 longitudinally.

Preferably, the constituent tapes are stacked in a single stack or in two or more parallel adjacent stacks. The latter normally requires one or two full width metal tapes to bridge from stack to stack. However, in some embodiments that bridging is achieved by one or two full width superconducting tapes. Structures with exactly two parallel stacks  
25 appear from preliminary experiments to have superior AC loss characteristics.

Preferably also, diffusion bonding between the superconducting tapes and metal tapes, if present, is obtained by assembling the tapes face to face and then heat treating them at a temperature at which diffusion between the metals occurs. However, it has been found that the temperature should be well controlled to minimise any deleterious  
30 effect on the superconducting material.

Good diffusion bonding between silver occurs at temperatures above 600°C. When the superconducting material has a typical BSCCO-2223 composition, bonding temperature should not exceed 842°C; and should not be around 780°C, at which rapid formation of detrimental secondary phases occurs. With this example, the preferred  
5 bonding temperature is in the range of 815°C to 825°C.

More preferably, the bonding is performed at a temperature below 700°C in an inert atmosphere or in a vacuum to avoid oxidation of the metal sheaths during the bonding process. Although a diffusion time of several hours will be required to achieve adequate bonding it is preferred to avoid excessively long diffusion times as they tend to  
10 produce too much sintering of the superconductor material.

Preferably, the diffusion bonded stack of tapes is rolled to reduce overall thickness and to strengthen the bonding.

According to another aspect of the invention there is provided a method of making a composite superconducting tape, the method comprising the steps of:

15 stacking a multiplicity of constituent monofilamentary or multifilamentary superconducting tapes together;

heat treating the stack of superconducting tapes to promote diffusion bonding;

and

rolling the diffusion bonded stack.

20 Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

25 Preferred embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a schematic cross-section of a composite superconducting tape according to the invention;

Figure 2 is a schematic cross-section of a second embodiment of a composite  
30 superconducting tape according to the invention corresponding to a tape of Figure 1 with the addition of a single outer metal tape;

Figure 3 is a cross-section of a third embodiment of a composite superconducting tape of the present invention corresponding to a tape of Figure 1 with the addition of two outer tapes;

Figure 4 illustrates a fourth embodiment of the invention and is a cross-section of a multi-column, composite superconducting tape of the present invention with single outer tape;

Figure 5 illustrates a fifth embodiment of the invention and is a cross-section of a multi-column, composite superconducting tape of the present invention with two outer tapes; and

Figure 6 is a cross-section of a sixth embodiment of a composite superconducting tape of the present invention, consisting of two multifilamentary superconducting tapes and two outer metal tapes.

#### **PREFERRED EMBODIMENT OF THE INVENTION**

The composite superconducting tape 1 shown in Figure 1 has a width of between 4.0 and 5.5 mm and a thickness of about 0.27 mm and comprises, for example, nine stacked monofilamentary tapes 2 bonded together. Each monofilamentary tape 2 comprises a filament 5 of superconducting material, for example, BSCCO-2223 in a silver/silver alloy cladding 7 as with known superconducting tapes. Typically (in the finished product as shown) each individual monofilamentary tape 2 has a thickness of 30µm and the filaments 5 themselves have typical thicknesses of 10 to 25µm.

To make the composite superconducting tape 1, the required number of monofilamentary tapes 2 must be made. The monofilamentary tapes 2 are made by firstly packing BSCCO-2223 oxide powder (or more usually a precursor convertible to the BSCCO-2223 composition by heat-treatment) into a cleaned and dry tube of silver or silver alloy having an internal diameter of approximately 8 mm and an external diameter of approximately 10 mm. A length of between 4 cm and 6 cm - depending upon the length of the silver tube - at one end of the tube is then swagged, and the tip of the swagged end closed off using smaller swagging dies, to prevent powder loss during packing. After swagging, the tube is again dried. The prepared tube is then carefully filled with the superconducting powder (precursor) under dry argon in a glove box. The powder is added small amounts at a time and tamped down with a silver rod until the

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tube is full, at which point the tube is closed off using a plug of silver tape. After the tube has been packed with superconducting powder and sealed, then the tube is degassed by placing it in a cool oven, in air, raising the temperature to 830°C and maintaining that temperature for five hours. The tube is then drawn in a number of stages down to a diameter of approximately 1.54 mm. The drawing is done in 23 steps in each of which the cross-sectional area of the tube is reduced by approximately 15%. During drawing, the tube is twice annealed at 500°C for between 30 and 60 seconds, when its diameter is 2.51 mm and 1.96 mm respectively.

The 1.54 mm wire is then rolled in a rolling mill in stages, to successive smaller thicknesses using roll gaps of 1.05, 0.80, 0.65, 0.50, 0.40, 0.35, 0.30, 0.25 and 0.22 mm, twice annealing for between 30 and 60 seconds at 500°C, at thicknesses of 0.65 mm and 0.35 mm.

The tape 2 is then cut into strips of equal length and stacked one upon each other and the stack 6 of tapes 2 wound on a former of ceramic material (with a ceramic paper strip interleaved to prevent bonding of turns). The tapes 2 are then heated at 820°C for about five hours to effect diffusion bonding and then, after it has cooled to room temperature, rolled in stages to 0.30 mm using successive roll gaps of 1.50, 1.30, 1.10, 0.95, 0.80, 0.65, 0.55, 0.45, 0.40, 0.35 and 0.30 mm and annealing under the same conditions as before at 1.10 mm and 0.65 mm.

The tape 1 is then heated in air, starting with a cool oven, to 840°C and held at that temperature for 50 hours, cooled to room temperature and rolled once on the same mill with a roll gap of 0.27 mm. Finally it is heat-treated in an atmosphere of 7.5% oxygen balance nitrogen, starting with a cold oven, heated to 825°C, held at that temperature for 40 hours and then cooled over a further period of 40 hours to 785°C. This heat-treatment regime serves to consolidate it, complete texturing and convert the precursor to the desired BSCCO-2223 phase without risking melting or any large volume fraction of the superconducting material.

The embodiment described above has used nine monofilamentary tapes 2 and a final thickness between 0.25 and 0.3 mm. However, more or fewer tapes can be used and the thickness varied depending upon the application of the composite superconducting tape 1, such as high load current carrying cables, its thickness and the extent

of subsequent rolling, and the relevant (but conflicting) requirements for capacity and flexibility. In most cases the balance of thicknesses and rolling reduction should be such that the filament thickness is generally in the range 10-40 $\mu$ m, but preferably close to the lower end of that range.

5 In an alternative embodiment, illustrated in Figure 3, the stack 1 has outer layers 3 and 4 of tapes of silver or silver alloy - typically comprising silver with 0.2% Magnesium - bonded to the two outer superconducting tapes. In this case, the outer layers 3 and 4 of silver or silver alloy about 0.22 mm thick are placed on the stack 6 of monofilamentary tapes 2 before the sintering and rolling processes and at the end of the  
10 process have thicknesses of about 25  $\mu$ m.

The outer layers 3 and 4 can be provided for a number of reasons.

Firstly, if the final composite tape is made sufficiently thin that the distance between the tape surface (metal/atmosphere) interface and the outermost silver or silver alloy/superconductor interface of silver cladding 7 becomes less than around 10 microns,  
15 then diffusion of the superconducting material to the tape surface occurs during the sintering process, which reduces the critical current density. If this is the case, then placing an extra layer of silver/silver alloy effectively increases the value of  $t_0$ , thereby removing this diffusion effect.

Secondly, outer layers 3 and/or 4 can be provided for mechanical reasons; if the  
20 material of the outer layer(s) is chosen to have a higher coefficient of thermal expansion than the superconductor tapes, it will put the filaments under compressive stress after the sintering process, which is beneficial for higher bending and tensile strain tolerance. In addition, it is possible to use a relatively strong tape (such as a silver alloy tape) on one side and a relatively weak one (such as pure silver one of similar thickness or a much  
25 thinner one) or in some cases none at all on the other side of the composite tape, so that the flexural neutral plane is displaced from its geometrical midplane towards the stronger tape. The result is that, when the tape is curved in such a direction that the side with the stronger tape (or the tape if there is only one) is convex, most of the filaments will be under compressive strain, which is less detrimental than tensile strain. This is useful,  
30 since in many applications the tape will be curved entirely in one direction.



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In a further development of the invention, multi-column tapes 10 can be provided, as illustrated schematically in Figures 4 and 5. As with the previous embodiments, outer layers 13 and 14 may be either of silver and/or silver alloy, or they might if desired be double-width superconducting tapes. Monofilamentary tapes 12 are  
5 stacked in two or more columns 15, and then all the layers 12, 13 and 14 bonded together and further processed in the same way as described with respect to the first embodiment. Preliminary experiments indicate that this columnar structure has lower AC losses than comparable single-column tapes, perhaps because the filaments decouple across the columns. It may be desirable to square the edges of the tapes (by  
10 trimming or otherwise) to minimise the risk of creating voids between the columns.

The tape of Figure 6 is consisted of two multifilamentary superconducting tapes 16 and two outer metal tapes 17 and 18. Multifilamentary superconducting tape is made by bundling the required number of monofilamentary tapes, putting them into another silver or silver alloy tube, drawing to smaller sized wire and the rolling to flat tape using  
15 similar procedure described with respect to the first embodiment.

Twisted (or untwisted) multifilamentary tapes, if desired with different numbers of filaments, different pitches and/or different twisting sense or direction, could also be stacked and bonded together and provided with or without the outer layers of silver/silver alloy.

20 Although the invention has been described with reference to specific examples it will be appreciated by those skilled in the art that it may be embodied in many other forms.